

Nitrate movement and removal along a shallow groundwater flow path in a riparian wetland within a sheep-grazed pastoral catchment: results of a tracer study

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Abstract The movement and removal of nitrate (NO_3^-) along a groundwater flow path within a riparian wetland was investigated during a 24-day period in late autumn–early winter, using a lithium bromide (LiBr)-potassium nitrate (KNO_3) tracer solution containing 19 200 mg/litre as Br^- and 193.8 mg/litre as NO_3^- -N. The tracer solution was added as an instantaneous dose of tracer solution at a depth of 10–20 cm to four injection wells in two 1 m² plots within a sheep-grazed pastoral catchment at the Whatawhata Agricultural Research Centre near Hamilton, New Zealand. Bromide and NO_3^- -N concentrations were measured periodically in: (1) wetland groundwater samples from piezometers installed at 15 and 30 cm depths and located at 30, 60, and 100 cm down gradient from the injection wells; and (2) surface flow samples. Peak concentrations of 50–250 mg/litre of Br^- and 0.2–1.1 mg/litre of NO_3^- -N were reached within 1–2 days after application at most piezometers. Nitrate concentrations decreased thereafter more sharply than did those of Br^- , resulting in decreased NO_3^- -N/ Br^- ratios from Days 2 through 7. More than 99% of groundwater samples collected after the tracer application had NO_3^- -N/ Br^- less than the value in the tracer solution indicating removal of NO_3^- -N during transport. Mass

flux estimates indicated removal of >90% of added NO_3^- -N along the 100 cm flow path from the injection, with essentially all of the NO_3^- removed within the first 30 cm of transport. On Days 10 and 24, just after rain events, surface flow from the experimental plots had greatly elevated NO_3^- -N concentrations that were not accompanied by correspondingly elevated Br^- concentrations, indicating that NO_3^- -N originating from the surrounding catchment was transported over the wetland surface with little penetration or mixing with wetland groundwater. Despite a significant capacity for NO_3^- -N removal from shallow groundwater equivalent to an annualised value of 50 kg/ha in these wetland study plots, large amounts of NO_3^- -N from the catchment are likely to move over the wetland surface during rain events without adequate soil contact time for efficient denitrification and retention.

Keywords riparian wetlands; nitrate removal; nitrate movement; groundwater; water quality; tracer study; grazing management

INTRODUCTION

The contribution of agricultural activities to nitrate (NO_3^-) loads in streams and rivers is a concern both in New Zealand (Smith et al. 1993; Ministry for the Environment 1997) and throughout the world (Naiman et al. 1995; Carpenter et al. 1998). In agricultural landscapes, wetlands can remove a significant proportion of the NO_3^- inputs originating from grazing animal excreta, fertiliser, and soil organic matter that would otherwise enter adjacent surface waters (Lowrance et al. 1984; Schipper et al. 1991; Nguyen et al. 1999a). To effectively manage wetlands in agricultural landscapes, however, more data are needed on wetland hydrology, soil-water contact time, and the minimum size and soil thickness necessary for a wetland to effectively remove NO_3^- and other nutrients from run-off (Gilliam 1994; Naiman & Decamps 1997; Burt et al. 1999). These issues are particularly relevant in New

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Zealand pastoral landscapes, where stock graze outdoors year round, and hence surface and subsurface run-off of nutrients from animal excreta to receiving waters may be high unless riparian wetlands and vegetated buffers can effectively remove these agricultural pollutants (Nguyen & Downes 1997, 1999).

Wetlands are typically highly productive ecosystems with soils that contain high levels of labile organic matter (Kadlec & Knight 1996; Nguyen et al. 1999a,b; Nguyen 2000). Shallow oxic groundwater rapidly becomes anoxic or suboxic as it moves through wetlands because decomposition processes vigorously consume available oxygen. Thus, wetlands typically have a strong capacity for removing NO_3^- from groundwater through denitrification (Seitzinger 1994; Hill 1996; Fennessy & Cronk 1997). Plant uptake and microbial immobilisation can also be important NO_3^- removal processes because the shallow water table generally present in wetlands allows groundwater NO_3^- to contact the root zone. The rate at which wetlands transform and cycle nitrogen (N) is dependent on factors such as the: organic carbon (C) content, C:N ratio, decomposition rate of soil organic matter, plant uptake rate of NO_3^- and ammonium (NH_4^+), flow rate of water through the wetland, and NO_3^- and NH_4^+ concentration of groundwater that discharges to the wetland (Hanson et al. 1994; Reddy & D'Angelo 1994; Fennessy & Cronk 1997). Because studies have generally reported significant removal of NO_3^- from groundwater during its transport through riparian wetlands (Lowrance et al. 1984; Johnston 1991; Gilliam 1994; Hill 1996), the protection, restoration, and creation of riparian wetlands is now a widely recommended management strategy to reduce the run-off of N from agricultural landscapes (Phipps & Crumpton 1994; Carpenter et al. 1998).

A variety of techniques have been applied to investigate NO_3^- movement and removal in riparian wetlands. Many studies have focused on quantifying NO_3^- removal by measuring the rates of processes such as denitrification in the laboratory (Seitzinger 1994; Groffman & Hanson 1997). *In situ* studies have compared NO_3^- movement in wetland groundwater to that of a more conservatively transported ion such as chloride or bromide (Br^-) (Jacobs & Gilliam 1985; Simmons et al. 1992; Nelson et al. 1995). Other *in situ* studies have focused exclusively on NO_3^- retention in surface flow by measuring the inflow and outflow rate of surface run-off (DeVito & Dillon 1993; Emmett et al. 1994). The addition of ^{15}N -labelled tracers has also been applied to the

study of NO_3^- retention and transformation in wetlands (Tiedje et al. 1981; Lindau et al. 1994). By measuring changes in the ^{15}N content of plants, soil, and gases, these studies have simultaneously provided data on the relative rates of several NO_3^- retention and transformation processes.

Quantifying the rates of NO_3^- removal in wetlands relative to the flow rate of groundwater through the wetland is a necessary step to develop sound wetland management strategies (Hill 1996). Despite an abundance of studies on the biogeochemical cycling of NO_3^- in wetlands, relatively few have examined *in situ* removal rates under natural hydraulic gradients. Further advances in our understanding of N cycling in wetlands will be dependent on a greater number of integrated hydrological and biogeochemical studies that provide accurate and detailed descriptions of hydrologic flow-path mechanisms in a variety of hydrogeologic settings (Gilliam 1994; Hill 1996).

In this study, we quantified the capacity of a riparian wetland to remove an instantaneous dose of tracer solution containing NO_3^- and Br^- through detailed vertical and lateral sampling of groundwater within *in situ* plots. The specific objective was to measure the rate of NO_3^- movement and removal in the shallow biologically active zone of the wetland soil during late autumn–early winter when surface and subsurface flow from agricultural catchments to riparian wetlands increases. A secondary objective was to determine the extent of surface–subsurface mixing within the wetland by sampling surface run-off in the wetland and examining changes in NO_3^- and Br^- concentrations with time over a 24-day period.

MATERIALS AND METHODS

Study site

The study site is located at the Whatawhata Research Centre (Quinn & Cooper 1997), 30 km west of Hamilton, New Zealand ($37^\circ 48'\text{S}$, $175^\circ 5'\text{E}$). The centre consists primarily of sheep-grazed ryegrass (*Lolium perenne*)-clover (*Trifolium repens*) pastures with hillslopes of $10\text{--}40^\circ$ and is considered to be typical of the farmable hill land located throughout the North Island of New Zealand (Farrelly 1986). The soil is predominantly Waingaro steepland soil, a northern yellow-brown earth (Umbric Dystrochrept, USDA Soil Taxonomy), derived from a sedimentary greywacke parent material (Bruce 1978). The soil has $<13\%$ amorphous minerals with

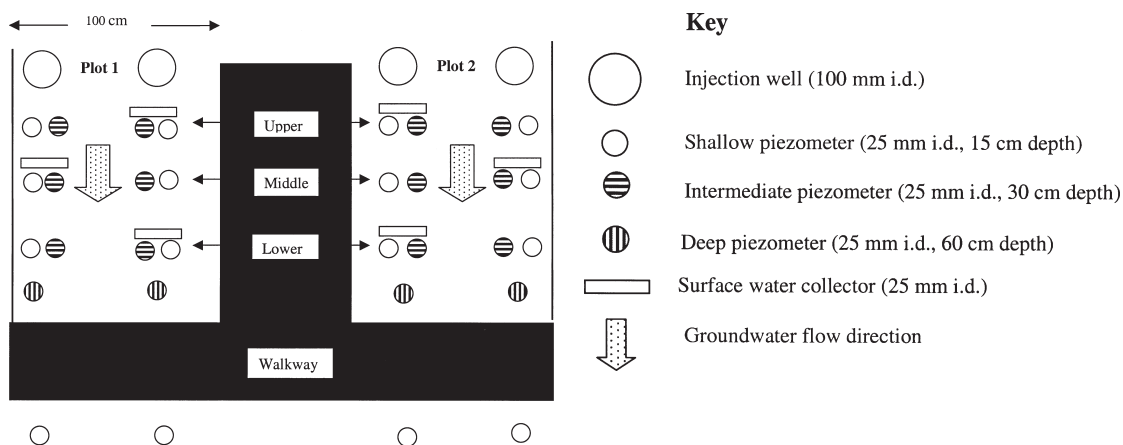


Fig. 1 Aerial view of the experimental plots showing locations of injection wells, sampling piezometers, and surface-water collectors.

a shallow (5–7.5 cm depth) clay loam topsoil of fine and medium nut structure, and a subsoil of firm clay with a weakly developed nut structure (Bruce 1978). Additionally, the soil has medium liquid and plastic limits of 57 and 49% (on a gravimetric basis) respectively, suggesting sensitivity to changes in soil moisture (Fieldes 1968a,b; Sheath & Carlson 1998).

The riparian wetland site (PW5) selected for this study is c. 350 m² (0.35 ha), located near the base of an ephemeral stream channel that drains a steep (10–30°) catchment (1.3 ha) and an upland wetland, just up stream from the location of its discharge into the Mangaotama River. This channel provides overland flow during and immediately following rainstorms that can be observed moving over the wetland surface. Data collected at this upstream site suggests that groundwater containing high NO₃⁻ concentrations discharges to the channel (Burns & Nguyen unpubl. data). The riparian wetland itself has a 10° slope, but does not have a defined stream channel running through it and run-off can be observed moving over the wetland surface as sheet flow (c. 1 cm deep) during heavy rainfall events. The downstream end of the wetland is located on a bank above the Mangaotama River and the wetland discharges directly into the river. The PW5 wetland soil has high root biomass (estimated root dry matter biomass of 15 780 kg/ha; F. Matheson pers. comm.) and organic matter content (42.5%; Nguyen et al. 1999b) to a depth of c. 20–30 cm. A dense bluish-grey clay of low permeability (aquiclude) is present in the soil at a depth of 50 cm.

Results from pump tests performed just before this study indicated mean values of groundwater

velocity of c. 300 cm/day at 10 cm depth, 33 cm/day at 30 cm depth, and <1 cm/day at 50 cm depth (J. C. Rutherford & L. Nguyen unpubl. data). During these pump tests and throughout the tracer study, the water table remained at or above the soil surface. Time-of-travel determined by measuring the conductivity of water samples (Schott Konduktometer CG855, cell constant = 0.38 cm⁻¹) after injection of LiBr tracer at arrays of piezometers screened over narrow depth intervals, confirmed that: (1) groundwater moves primarily in a lateral direction parallel to the 10° slope of the wetland surface; and (2) flow rates are rapid near the surface and decline sharply with depth (J. C. Rutherford unpubl. data).

Wetland vegetation consists mainly of floating sweet grass (*Glyceria declinata*), with <15% of vegetation as jointed rush (*Juncus articulatus*), sedge (*Carex* sp.), and lotus (*Lotus pedunculatis*). The study plots within the wetland were almost exclusively composed of floating sweet grass.

The climate in the study area is classified as humid temperate with a mean annual temperature of 13.7°C and mean annual rainfall of 161.4 cm (1952–92 mean). The study was carried out over a 24-day period (24 May–18 June) during the late autumn–early winter of 1999. Shallow groundwater temperature in the wetland ranged from 10 to 12°C during the study.

Plot and piezometer installations

Two independent replicate 100 × 100 cm plots were established in the PW5 wetland. Lateral walls of polyvinyl chloride (PVC) were installed to a depth of c. 60 cm parallel to the slope of the land surface

(and the groundwater flow direction) in each plot. Two holes (10 cm internal diam. (i.d.) \times 20 cm deep) were excavated so that the mid-point was at the upslope end of each plot and 20 cm from the nearest wall (Fig. 1). A 10 cm i.d. PVC pipe was placed into each of the holes to a depth of 10 cm, so that tracer solution could be injected into the open hole over a depth interval of 10–20 cm below the land surface.

Thirty-two PVC piezometers (2.5 cm i.d. PVC pipes which were screened over the lowest 12 cm with 0.025 cm slots and covered with permeable fabric to minimise clogging) were installed downslope from each injection well as shown in Fig. 1. Piezometers were installed by making an auger hole 5 cm in diameter to the required depth, placing the piezometer into the hole, pouring quartz drilling sand into the remaining space, and then sealing the top of the hole with bentonite. In each of the two plots, piezometers were installed at different depths as follows: (1) six piezometers at a depth of 15 cm (mid-point of screen) and located 30 cm (two piezometers), 60 cm (two piezometers), and 100 cm (two piezometers) from the injection well. These are referred to as the upper-shallow, middle-shallow, and lower-shallow piezometers, respectively; (2) six piezometers at a depth of 30 cm immediately adjacent (c. 5 cm away) to those described above. These are referred to as the upper-intermediate, middle-intermediate, and lower-intermediate piezometers, respectively; (3) two piezometers at a depth of 60 cm and located 130 cm downslope from the injection well; and (4) two piezometers at a depth of 15 cm and located 180 cm downslope from the injection well.

The plot layout was designed so that two flow paths (from each of the two injection wells) were sampled in each plot at each of the three piezometer locations—upper, middle, and lower (30, 60, and 100 cm distance from the injection wells), and at two depths—shallow and intermediate (15 and 30 cm) (Fig. 1). Complete independence of the two flow paths could not be conclusively demonstrated, because of possible lateral dispersion and mixing of the tracer plumes. However, each of the samples from the two piezometers at a given depth and flow path position in each plot can be treated as independent measurements of each of the two plumes, even in the presence of some plume mixing. The net result was two samples of NO_3^- and Br^- concentrations at a given depth and flow path position for each replicate plot in the study wetland.

Three PVC surface run-off collectors (3.2 cm i.d.) 15 cm in length, capped at each end, and covered with

permeable fabric were installed in each plot as shown in Fig. 1. Each collector was installed lengthwise, so that the bottom half of the pipe was at a depth of 1.6 cm below the land surface, whereas the top half of the pipe (screened over the entire 15 cm length with 0.025 cm slots) was located above the land surface.

Tracer solution

The tracer solution consisted of LiBr (19 200 mg/litre Br^-) and KNO_3 (193.8 mg/litre NO_3^- -N). The NO_3^- -N/ Br^- (mass) ratio of the tracer solution was 0.01. Such high concentrations of the tracers were chosen to insure that Br^- and NO_3^- could be discerned from background concentrations once the tracer mixed with the native groundwater of the wetland. Before adding the tracer to each injection well, one well volume of water was removed and discarded, and a volume of tracer solution equivalent to the amount occupied by the 10–20 cm depth increment in the well (860 ml) was then immediately added as an instantaneous dose to each injection well. The total amounts of NO_3^- -N and Br^- added to each well were 166.6 and 16 512 mg, respectively.

Sampling of groundwater and surface flow

Groundwater samples (175 ml) were collected from each piezometer with a syringe just before the tracer injection—Day 0 (24 May), and at Days 1, 2, 4, 7, 10, 15, and 24 after the tracer injection (25, 26, 28, and 31 May and 3, 8, and 17 June, respectively). One well volume was first removed from each piezometer, and c. 1–1.5 h of recovery time was allowed before collecting the sample. The surface water collectors were sampled without any prior removal of water. Additionally, a sample of surface outflow from the wetland was collected at a square-notch weir just above where the wetland outflow entered the Mangaotama River (c. 15 m downslope from the plots).

Hydrologic measurements

Precipitation was measured in a tipping bucket rain gauge located c. 1 km from the study wetland. Stream stage was measured every 15 min through a v-notch weir at a gauge site on the Mangaotama River c. 200 m up stream from where the wetland discharges into the river. Stream flow was determined by relating each stage measurement to a discharge value through a rating curve. Wetland outflow was measured volumetrically on 17 occasions from March through August 1999 at the square notch weir where wetland outflow samples were collected. Wetland outflow was highly correlated

with discharge of the Mangaotama River ($r^2 = 0.98$), indicating that the continuous discharge record at the river could be used to infer wetland discharge.

Laboratory analyses

Groundwater samples were passed through GFC filters (1 μm pore size) before analysis. Samples were stored at 4°C until Br^- analysis (10 days), and at 0°C until NO_3^- analysis (<5 days). Bromide was analysed by inductively coupled plasma emission spectroscopy-mass spectrometry at RJ Hill Laboratories in Hamilton, New Zealand. Nitrate was analysed by a cadmium column reduction method after complexation with 1-naphthyl-ethylenediamine followed by analysis on an auto-analyser at the NIWA-Hamilton laboratory (APHA 1989). Additionally, all groundwater and surface water samples were screened by measuring specific conductance. The screening was conducted to decide which samples were likely to have Br^- concentrations sufficient to justify chemical analysis.

NO_3^- retention calculations

Nitrate removal rates were estimated by using the Br^- and NO_3^- analyses in combination with calculations of groundwater flow rates for each distance travelled through the experimental plots. A control volume was defined through which NO_3^- removal was considered (Hemond & Fechner 1994; Nelson et al. 1995). The approach used here is similar to that of Nelson et al. (1995). First, the mass of soil within the control volume was calculated:

$$M_s = A \times L \times P_b \quad (1)$$

where: M_s = mass of soil in the control volume (kg); A = cross-sectional area of the control volume (m^2); L = length of flow between the injection well and monitoring piezometer (m); and P_b = bulk density of soil in the control volume (250 kg/m^3).

The cross-sectional area was determined by multiplying the width of the open hole from which the tracer was added (10 cm) times the combined depth from the top of the screen of the shallow piezometer to the bottom of the screen of the intermediate depth piezometer (27 cm).

The daily groundwater flow rate during the experiment was calculated as follows:

$$Q = V \times n \times A \quad (2)$$

where: Q = daily flow rate (m^3/day); V = pore water velocity (m/day); and n = effective porosity.

Mass fluxes of Br^- and $\text{NO}_3\text{-N}$ were estimated for the 24-day study period by assuming the mean time-to-peak of Br^- concentrations was representative of

the groundwater flow velocity. These mass fluxes are only estimates because of the simplifying assumption necessary to make the calculation that Br^- was transported conservatively with groundwater flow. Bromide has low biological and chemical reactivity in soil environments, and therefore, has commonly been used as a conservative hydrologic tracer (Germann et al. 1984; Jabro et al. 1991; Simmons et al. 1992). Additionally, Br^- is transported in a manner similar to NO_3^- , and thus is a good surrogate for NO_3^- transport in the absence of biogeochemical processes (Smith & Davis 1974). Bromide has low reactivity relative to that of other solute tracers (Netter & Behrens 1992), however, Br^- can be taken up by plants during tracer studies in which transport occurs through the rooting zone (Kung 1990; Schnabel et al. 1995). To minimise Br^- uptake by plants, this study was completed within a short time interval of 24 days during the late autumn–early winter.

The time-to-peak values ranged from 2–4 days among all of the piezometers, yielding an estimated groundwater flow velocity of 7.5–30 cm/day. The results of pump tests indicated that the values of saturated hydraulic conductivity (K_s) at 12.5 and 30 cm depth were 300 and 80 cm/day, respectively (J. C. Rutherford & L. Nguyen unpubl. data). Soil porosity was 0.88 for the 0–30 cm depth interval, and 0.77 for the 30–60 cm depth interval. By multiplying K_s values with the head gradient in the wetland of 0.1 and dividing by the soil porosity, estimated groundwater flow velocities at 12.5 and 30 cm depth are 34 and 9 cm/day, respectively, in good agreement with the range of groundwater flow velocities (7.5–30 cm/day) calculated from the Br^- tracer data, and providing additional confirmation of the assumption of conservative transport.

A theoretical daily mass flux of NO_3^- was calculated for each flow path distance from the tracer injection as follows:

$$M\text{-NO}_3^-_{\text{theoret.}} = (\text{Br}^- \times T) \times Q \quad (3)$$

where: $M\text{-NO}_3^-_{\text{theoret.}}$ = daily mass flux of NO_3^- in the absence of biogeochemical processes; Br^- = daily concentration of bromide; and T = mass ratio of $\text{NO}_3^-/\text{Br}^-$ in tracer solution (0.01).

The theoretical mass flux of NO_3^- was then subtracted from the actual mass flux to calculate NO_3^- removal as follows:

$$MR\text{-NO}_3^- = M\text{-NO}_3^-_{\text{theoret.}} - M\text{-NO}_3^-_{\text{actual}} \quad (4)$$

where: $MR\text{-NO}_3^-$ = mass of NO_3^- removed daily; and $M\text{-NO}_3^-_{\text{actual}}$ = measured daily mass flux of NO_3^- .

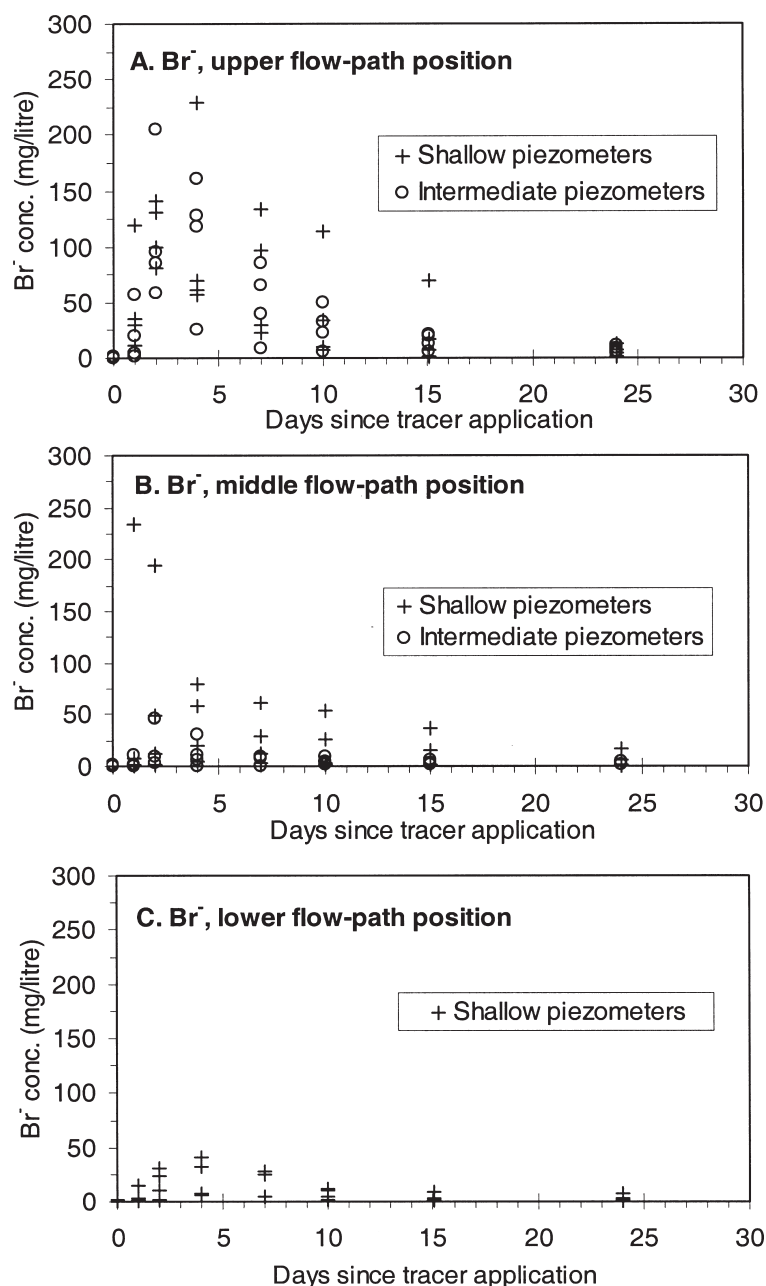
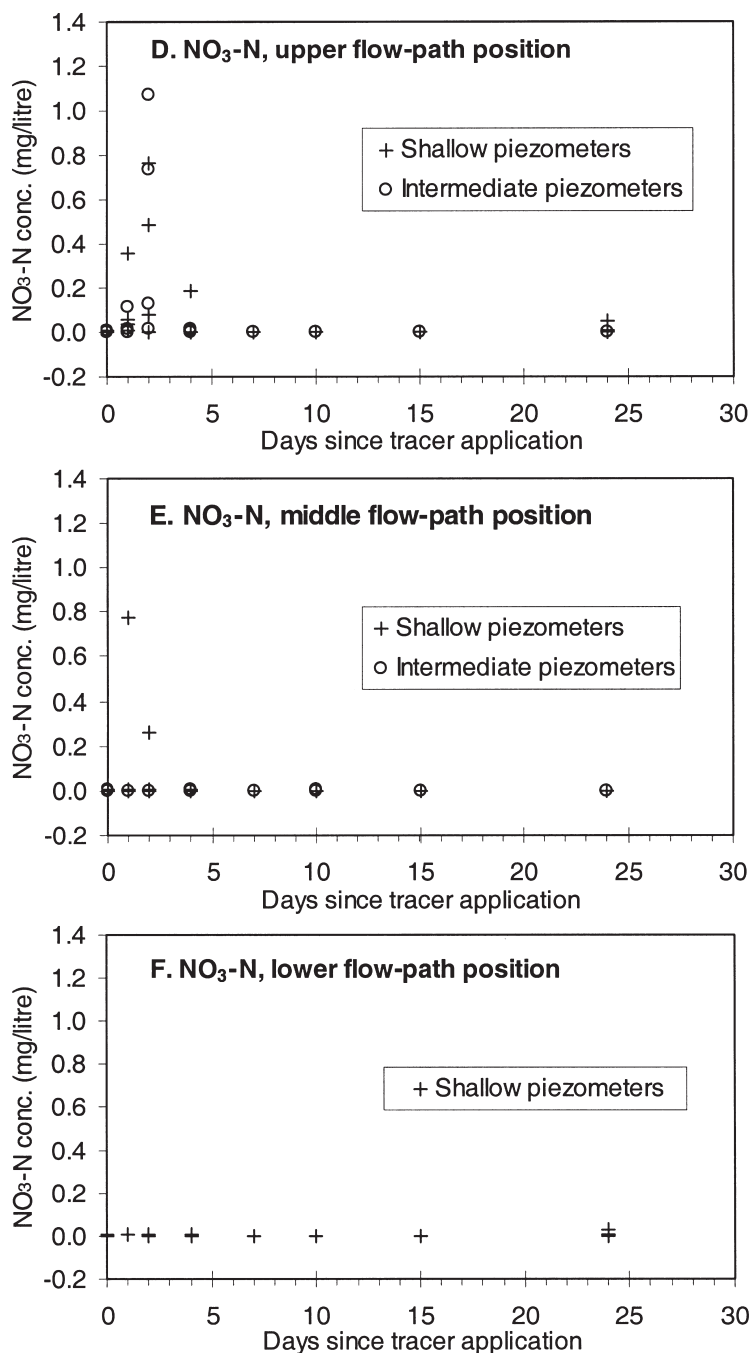


Fig. 2 Concentrations of Br⁻ in piezometers at the **A**, upper, **B**, middle, and **C**, lower flow-path positions; and concentrations of NO₃-N in piezometers at the **D**, upper, **E**, middle, and **F**, lower flow-path positions during the 24-day tracer study.

Daily concentrations of Br⁻ and NO₃⁻ were estimated through linear interpolation of the samples collected on Days 1, 2, 4, 7, 10, 15, and 24. The mean concentration of four shallow and four intermediate piezometers was used to calculate mass flux and removal for each distance along the flow path. The

mass flux of Br⁻ within the control volume was not expected to equal the total amount of Br⁻ added because of spreading of the tracer plume beyond the bounds of the control volume through diffusion and dispersion. Additionally, any uptake of Br⁻ by plants would result in an underestimation of NO₃⁻ removal rates.

Fig. 2 *continued*

RESULTS

Groundwater and surface run-off chemistry

On Day 0 before the application of the tracer solution, background NO₃-N and Br⁻ concentrations in groundwater and surface water samples at all sites

were <0.01 and 1 mg/litre, respectively (Fig. 2). One day after tracer application, NO₃⁻ and Br⁻ concentrations increased significantly at many of the sampling sites indicating that the tracer solution moved rapidly through the subsurface. The highest NO₃⁻ and Br⁻ concentrations were generally

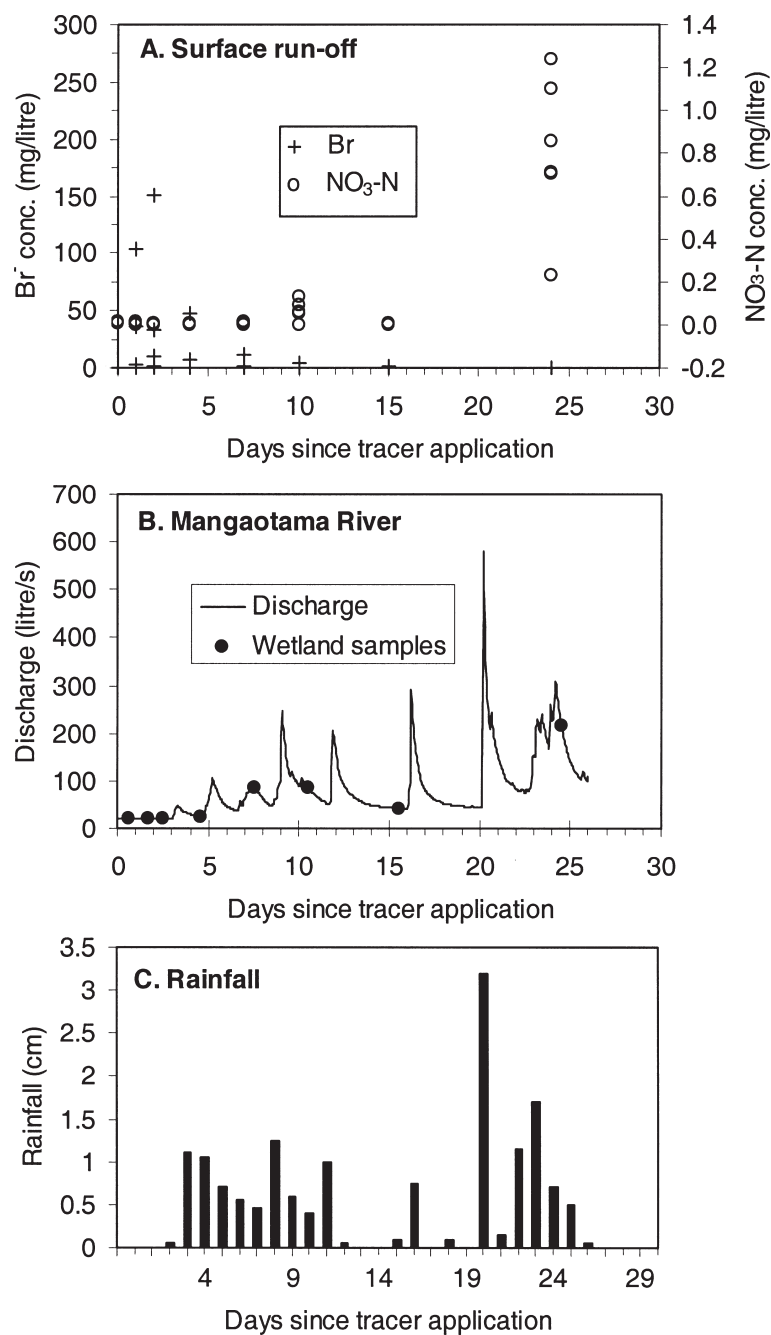


Fig. 3 A, Concentrations of Br⁻ and NO₃-N in surface run-off collectors; B, discharge of the Mangaotama River with wetland sample times located on hydrograph; and C, rainfall amounts during the 24-day tracer study.

observed within 1–2 days after the application of the tracer solution, but Br⁻ concentrations did not peak at some piezometers until Day 4 (Fig. 2). The highest concentrations of these solutes were generally measured in the upper-shallow, middle-shallow, and upper-intermediate piezometers.

Three sets of samples collected during the experiment are not presented: (1) deep piezometers (60 cm depth) at 130 cm down gradient from the injection well; (2) shallow piezometers at 180 cm down gradient from the injection well; and (3) the wetland outlet. All of these samples are considered

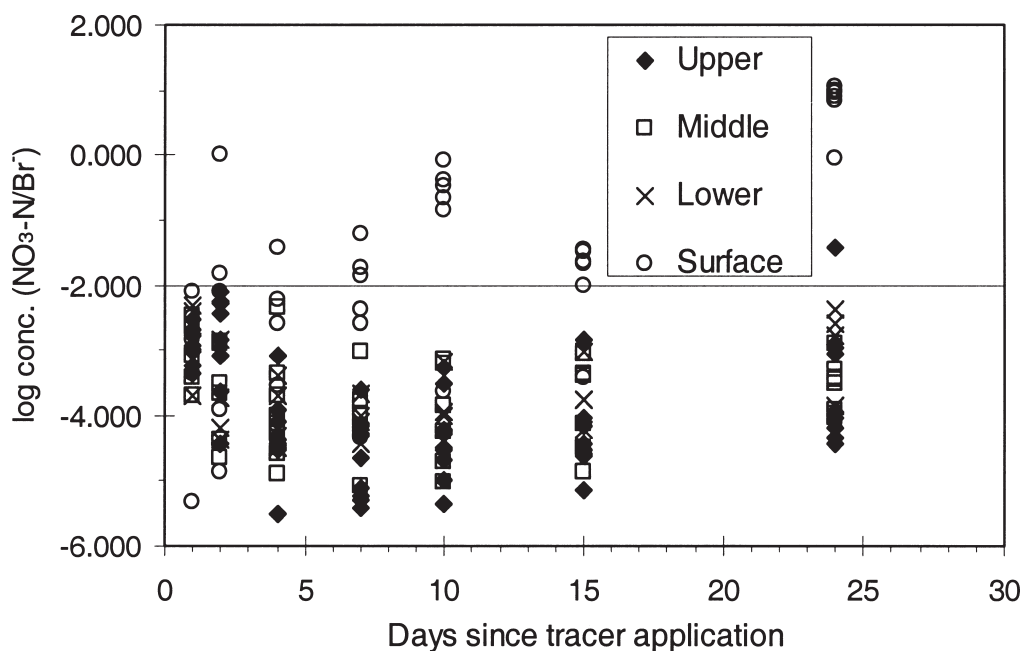


Fig. 4 Ratios of log $\text{NO}_3\text{-N}/\text{Br}^-$ concentration at the upper, middle, and lower flow-path positions, and in surface run-off collectors. Horizontal line at log $\text{NO}_3\text{-N}/\text{Br}^-$ concentration ratio of -2 represents the ratio of the two constituents in the applied tracer solution.

to have negligible concentrations of Br^- because conductance measurements suggested that little of the tracer reached these sites during the 24-day study. Only samples collected at these sites on Day 4 were analysed for $\text{NO}_3\text{-N}$ and Br^- , and concentrations were generally <0.005 and <10 mg/litre, respectively, confirming that little of the tracer was present on that day.

Nitrate concentrations were elevated in the surface water collectors on Day 24—the highest NO_3^- concentrations measured during the experiment, and slightly elevated on Day 10 (Fig. 3A). In contrast, Br^- concentrations were not similarly elevated in surface waters on these two sampling days.

River and wetland discharge

Total precipitation during the 24-day tracer experiment was 14.4 cm, resulting in a series of eight hydrograph peaks at the Mangaotama River (Fig. 3B). The greatest discharge recorded in the Mangaotama River during the tracer experiment was c. 580 litres/s on Day 20 in response to a 3.2 cm rain event. The groundwater samples were collected at a range of river, and hence wetland discharges (Fig. 3B). For example, wetland and river discharges were 1 and 216 litres/s, respectively, at the time of

groundwater sample collection on Day 24; the highest values of any samples collected throughout the study. At that time, the river and wetland were receding from a 1.7 cm rain event on the previous day. Additionally, the groundwater samples on Days 7 and 10 were also collected at a time of slightly elevated river discharge of c. 86 litres/s. All other samples were collected at base flow conditions when river discharge was <50 litres/s and wetland discharge was <0.15 litres/s.

Evidence of NO_3^- removal from groundwater

Changes in the $\text{NO}_3\text{-N}/\text{Br}^-$ concentration ratio (as expressed by log $\text{NO}_3\text{-N}/\text{Br}^-$ concentration) with time in the wetland piezometers indicate the relative source/sink behaviour of NO_3^- (Fig. 4). This ratio was generally less than that (-2) present in the applied tracer solution, except for elevated values in samples from surface collectors. The most surface run-off samples with the highest values of log $\text{NO}_3\text{-N}/\text{Br}^-$ concentration were found on Days 10 and 24. Most groundwater samples had $\text{NO}_3\text{-N}$ concentrations an order of magnitude or more below the conservative mixing line, indicating removal of a large proportion of $\text{NO}_3\text{-N}$ from groundwater flow. The only groundwater sample with a log $\text{NO}_3\text{-N}/\text{Br}^-$

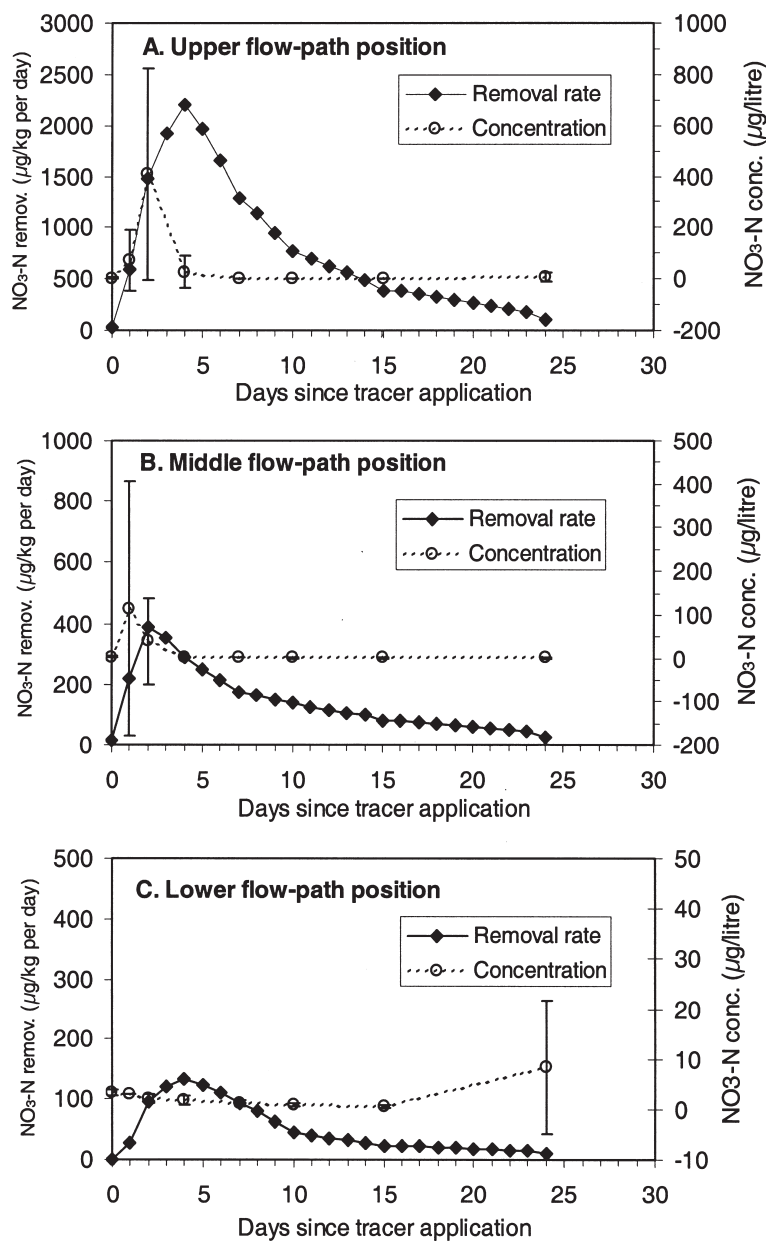


Fig. 5 Mean $\text{NO}_3\text{-N}$ concentration and removal rate for piezometers at the **A**, upper; **B**, middle; and **C**, lower flow-path positions. Error bars represent the standard deviation of the mean concentration of each of the four samples collected at each flowpath position.

concentration ratio greater than -2 was from a shallow piezometer on Day 24, the same day on which the highest wetland discharge was recorded.

Removal rate of $\text{NO}_3\text{-N}$ at different flow path positions

The $\text{NO}_3\text{-N}$ removal rate in piezometers was dependent on flow path position (Fig. 5). At the upper flow-path position, the mean $\text{NO}_3\text{-N}$ removal

rate increased sharply during the first 4 days of the experiment, and reached a peak value of $>2000 \mu\text{g/kg per day}$ on Day 4. The removal rate then decreased as rapidly as it had previously increased through Day 7 before decreasing progressively more gradually thereafter. On Day 15, the $\text{NO}_3\text{-N}$ removal rate was still c. $400 \mu\text{g/kg per day}$. The mean $\text{NO}_3\text{-N}$ concentration at the upper flow-path position rose even more sharply than the removal rate, peaking on

Day 2 at c. 400 $\mu\text{g}/\text{litre}$, then decreased just as sharply to c. 50 $\mu\text{g}/\text{litre}$ by Day 4.

At the middle flow-path position, the mean $\text{NO}_3\text{-N}$ removal rate rose sharply during the first 2 days of the tracer experiment, and peaked on Day 2, two days before the peak at the upper flow-path position (Fig. 5B). The peak removal rate was c. 400 $\mu\text{g}/\text{kg}$ per day, <25% of the peak removal rate at the upper flow-path position, and decreased in a nearly exponential manner through the end of the experiment. The mean $\text{NO}_3\text{-N}$ concentration reached a peak value of c. 100 $\mu\text{g}/\text{litre}$ on Day 1 of the experiment, 1 day before the removal rate reached a peak value, and declined to <5 $\mu\text{g}/\text{litre}$ by Day 4.

The pattern of change in the $\text{NO}_3\text{-N}$ removal rate at the lower flow-path piezometers was similar to that at the upper flow-path piezometers except the peak value on Day 4 was only c. 125 $\mu\text{g}/\text{kg}$ per day, which is c. 5% of the value at the upper flow-path piezometers (Fig. 5C). The mean $\text{NO}_3\text{-N}$ concentration, however, did not increase early in the experiment as observed at the other piezometer locations. As shown, the mean $\text{NO}_3\text{-N}$ concentrations actually decreased during the first 2 days of the experiment, and remained <5 $\mu\text{g}/\text{litre}$ until increasing slightly to 8 $\mu\text{g}/\text{litre}$ on Day 24.

For all 20 piezometers that were sampled routinely during the tracer study, and for which data are reported here, there was a sharp increase beginning on Day 7 in the number of samples that had $\text{NO}_3\text{-N}$ concentrations <1 $\mu\text{g}/\text{litre}$, the method detection limit. The number of non-detects increased from 5% of groundwater samples on Day 2, to 20% on Day 4, and then remained >50% for all sampling dates through the remainder of the study.

The percent removal of $\text{NO}_3\text{-N}$ for the entire 24-day experiment as calculated with Equation 4 was equivalent to c. 92% of added $\text{NO}_3\text{-N}$ within the 100 cm flow path in the experimental plots, and essentially all of the removal occurred within the first 30 cm of the flow path (Table 1). Even during Days 1–4, when $\text{NO}_3\text{-N}$ concentrations reached their highest values, most (96%) of the $\text{NO}_3\text{-N}$ was removed within the 100 cm flow path. Removal from 30–100 cm along the flow path was greatest during Days 1–4, and then little $\text{NO}_3\text{-N}$ was removed through this part of the subsurface during the remainder of the experiment.

DISCUSSION

Wetlands plots as a sink for the applied NO_3^- tracer

Results obtained (Table 1) strongly indicate that the vast majority of the $\text{NO}_3\text{-N}$ added in the tracer solution was removed during groundwater transport through biogeochemical processes such as denitrification, microbial immobilisation, and plant uptake (Hill 1996; Fennessy & Cronk 1997). The study wetland was previously found to have a high denitrification enzyme activity of $5.72 \pm 1.84 \mu\text{g N}_2\text{O-N/g soil per h}$ (Nguyen et al. 1999b), so it is likely that much of the $\text{NO}_3\text{-N}$ removal from groundwater during the 24-day study period can be attributed to denitrification.

Most of the log $\text{NO}_3\text{-N}/\text{Br}^-$ concentration ratios were less than that of the tracer solution, and 89% of the samples collected fell below the conservative mixing line (Fig. 4) indicating active $\text{NO}_3\text{-N}$ removal

Table 1 Percent removal of $\text{NO}_3\text{-N}$ (relative to the sum of the removal and the mass flux) for each flow path interval and for the total flow path over the first 4 days and over the 24-day tracer experiment. Values in parentheses represent the standard deviation of the mean for each time interval.

Flow path interval*	Removal (%) [†]	
	Day 1–4	24-day
Injection–upper	69.9 (16.1)	93.0 (13.8)
Upper–middle	13.6 (14.3)	1.4 (7.4)
Middle–lower	12.7 (11.7)	–2.3 (8.9)
Total flow path	96.2 (4.4)	92.1 (14.4)

*Upper, middle, and lower flow paths represent piezometer locations at 30, 60, and 100 cm from the injection wells, respectively. [†]Data are extrapolated from eight samples collected at each flow path position on Days 1, 2, 4, 7, 10, 15, and 24 as discussed in text.

from flowing groundwater. If only the groundwater samples are considered, then >99% of the samples had log $\text{NO}_3\text{-N}/\text{Br}^-$ concentrations that fell below the conservative mixing line. The concentrations of $\text{NO}_3\text{-N}$ in piezometers decreased more sharply than did those of Br^- from Days 2 to 7 of the experiment indicating that this was a time period of strong $\text{NO}_3\text{-N}$ losses from solution. These sharp decreases in $\text{NO}_3\text{-N}$ concentrations were initially coincident with increases in the $\text{NO}_3\text{-N}$ removal rate, which peaked later than the $\text{NO}_3\text{-N}$ concentrations at all three flow-path positions. Mass balance estimates show that <10% of the added $\text{NO}_3\text{-N}$ was transported as far as the second set of piezometers, 60 cm from the injection wells. In total, more than 92% of the added $\text{NO}_3\text{-N}$ was removed from groundwater within the 100×100 cm plots. The consistently low $\text{NO}_3\text{-N}$ concentrations at the lower flow-path position 100 cm from the injection well attests to the nearly complete removal of $\text{NO}_3\text{-N}$ along the groundwater flow path in the plots.

The results of this study are consistent with those of many natural gradient and applied tracer studies showing strong NO_3^- removal in riparian zones (Peterjohn & Correll 1984; Cooper 1990; Simmons et al. 1992; Haycock & Pinay 1993). Most studies of NO_3^- in riparian zones have examined removal from subsurface waters over distances of several metres, however, in this study, we have demonstrated almost complete removal in the subsurface of 333.3 mg of $\text{NO}_3\text{-N}$ within replicate 100×100 cm plots over a 24-day period. This measured removal rate is equivalent to an annual removal rate of c. 50 kg/ha, comparable to values that have been reported for riparian sites in Maryland, United States (Peterjohn & Correll 1984; Jordan et al. 1993), but less than those reported for a riparian wetland in Denmark (Brusch & Nilsson 1993). Many of the samples collected from Days 7 to 24 during the experiment had low $\text{NO}_3\text{-N}$ concentrations at or near method detection limits (Fig. 2D–F), suggesting that the potential denitrification rate and hence $\text{NO}_3\text{-N}$ removal rate was probably restricted by the lack of $\text{NO}_3\text{-N}$. Thus, it is likely that the studied wetland soil is capable of removing much larger applications of NO_3^- over short transport distances than the amount of NO_3^- applied (50 kg/ha) in this study, suggesting that the estimated removal rate of 50 kg/ha per year is conservative. Additionally, because the tracer experiment was carried out during late autumn–early winter, NO_3^- removal rates may be higher during the active growing season, when groundwater temperatures are higher and vegetation growth rates are greater.

Sources of NO_3^- to surface water collectors

The elevated $\text{NO}_3\text{-N}$ concentrations measured in the surface collectors on Days 10 and 24 were not accompanied by elevated Br^- concentrations. On these two dates, the samples from the surface water collectors yielded the highest $\text{NO}_3\text{-N}/\text{Br}^-$ ratios of the study. Nitrate concentrations in these samples were greater than could be accounted for by conservative mixing of the Br^- in the tracer solution. Additionally, the inferred values of wetland discharge on these two sampling days were the highest of any of the sampling days during the experiment. These data strongly suggest that the elevated $\text{NO}_3\text{-N}$ concentrations measured in these surface water collectors on Days 10 and 24 originated not from the tracer solution, but from the surrounding wetland catchment. In contrast to the surface water samples, only 1 out of the 24 samples of shallow groundwater (15 cm depth) collected on Days 10 and 24 had a $\text{NO}_3\text{-N}/\text{Br}^-$ ratio greater than that of the tracer solution, indicating that NO_3^- from the surrounding catchment was not generally present in shallow groundwater. On these dates, when samples were collected during the hydrograph recession after the cessation of rainfall, the NO_3^- inputs originating from the agricultural catchment moved largely over the wetland surface and did not greatly penetrate to depth.

Excess $\text{NO}_3\text{-N}$ was also present in some of the surface water collectors on Days 1, 2, 4, 7, and 15, suggesting that NO_3^- from the surrounding catchment was probably present in the surface water collectors on these sampling days as well. At the time of sampling on Day 7, stream flow (and by inference, wetland outflow) in the Mangaotama River was at an elevated value of 86 litres/s, similar to the value at the time of sampling on Day 10. However, base flow conditions prevailed on Days 1, 2, 4, and 15 indicating that some NO_3^- from the surrounding catchment is generally always present at some of the sampling locations of surface flow.

The finding of significant $\text{NO}_3\text{-N}$ concentrations in surface water in the study wetland during the tracer experiment is consistent with results of studies of a riparian wetland in Ontario, Canada in which little NO_3^- was retained because groundwater flowed over the wetland surface, limiting residence time and interaction with organic soils (Warwick & Hill 1988; Hill 1991). Despite efficient removal of NO_3^- in the shallow subsurface of the study wetland, significant bypassing of the soils by surface run-off during and after rain events is likely to limit NO_3^- retention capacity. Because frequent small rainstorms are characteristic of the climate at the Whatawhata

Agricultural Research Centre in the North Island of New Zealand (and indeed throughout New Zealand), run-off that bypasses the NO_3^- retention capacity of riparian wetlands by moving directly to streams over the surface of these wetlands is likely to play an important role in transporting NO_3^- to streams and rivers. Management strategies that seek to minimise the run-off of NO_3^- into surface waters in New Zealand should consider approaches that minimise a decline in subsurface hydraulic conductivity as a result of soil compaction such as limiting sheep and cattle treading close to wetlands and in important hydrologic source areas for storm run-off. Cattle treading during winter months for a short duration (2–3 days) on this soil type significantly reduce the infiltration rate and soil macroporosity (Nguyen et al. 1998).

SUMMARY

Following the application of a tracer solution containing LiBr and KNO_3 to a series of wells installed within replicate 1 m^2 experimental plots at a riparian wetland at the Whatawhata Research site, Br^- and $\text{NO}_3\text{-N}$ concentrations increased rapidly and reached peak values within 1–4 days. Solute concentration peaks generally became smaller in a horizontal direction down gradient from the injection wells, and a lag of 2 days in peak Br^- concentrations was evident in the shallow piezometers between 30 and 100 cm down gradient from the tracer injection.

Nearly all the groundwater samples had lower $\text{NO}_3\text{-N}$ concentrations than would be expected based on conservative mixing of the tracer solution, indicating a loss of NO_3^- from groundwater during transport through the wetland subsurface. These losses were greatest from Days 2 through 7 when $\text{NO}_3\text{-N}$ removal rates were highest and abundant $\text{NO}_3\text{-N}$ was available. The % removal rate of $\text{NO}_3\text{-N}$ was greatest closest to the injection wells, and then declined down gradient thereafter. About 92% of the $\text{NO}_3\text{-N}$ added as tracer was removed within 100 cm of the injection wells, and essentially all of this removal occurred within the first 30 cm of groundwater transport.

Samples of surface flow showed little evidence of the applied tracer solution, but $\text{NO}_3\text{-N}$ concentrations were greatly elevated on Days 10 and 24 in response to elevated discharge from the wetland, and slightly elevated in some of the surface flow collectors on the other sampling dates. Because increased Br^- concentrations did not accompany the increased

$\text{NO}_3\text{-N}$ concentrations, the NO_3^- probably originated from outside the wetland study plots in run-off from the surrounding catchment. The results of this study indicate that consideration of factors such as treading by grazing animals that may enhance surface run-off from riparian wetland catchments are important in any comprehensive management strategy that seeks to minimise NO_3^- run-off to surface waters.

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